Supplementary Information

Spontaneous Oxidation of I⁻ in Water Microdroplets and its Atmospheric Implications

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**Experimental Methods**

**Chemicals and Materials**

Sodium iodide, sodium bromide, sodium chloride, and sodium fluoride were purchased from Shanghai Macklin Biochemical Co., Ltd. Milli-Q water (18.2 MΩ·cm⁻¹) used for all experiments was obtained from a Purelab Quest system (ELGA LabWater, UK). Various concentrations of NaI solutions were prepared just before use.

**Generation of microdroplets and mass spectrometric analyses**

A schematic drawing of the experimental setup for the microdroplet reactions is provided in Fig. 1a. Solutions were sprayed to generate microdroplets by using a syringe pump at 5 µL/min flow rate with high purity nitrogen at a varied high pressure as the nebulizing gas. The inner diameter (I.D.) of the fused silica capillary used for spraying is 100 µm. Unlike electrospray ionization, no voltage was applied to the solutions. The distance between the tip of the silica capillary and the mass spectrometer inlet could be changed and was defined as the reaction distance. The products were detected and analyzed by an LTQ-XL mass spectrometer (Thermo-Fisher, Waltham, MA). The tube lens voltage of the mass spectrometer was set as 0 V in all of the experiments to avoid unwanted fragmentation of the ions. Collision-induced dissociation (CID) was also performed for the structural analysis of the products. All these experiments were carried out under atmospheric pressure.

The spray experiment was also repeated by replacing the silica capillary with a stainless steel capillary that was grounded or biased between -22 V to +22 V by a DC power supply to rule out the possibility of contact electrification between the silica capillary and the water solutions.

The solutions of NaF, NaCl, and NaBr were also sprayed under the same conditions as those of NaI, but no oxidation products were observed in these systems.

**Collection of microdroplets and ultraviolet-visible absorption measurements**

As depicted in Figure 2, microdroplets of the sprayed NaI solution were collected in a beaker pre-filled with some water to avoid fast drying. The ultraviolet-visible (UV-Vis) absorption spectrum of the collected solution was determined using a spectrophotometer (SPECORD 210 PLUS, Analytik Jena) at room temperature.
Figure S1. The mass spectra showing concentration-dependence of the spontaneous oxidation of I⁻ supporting the data presented in Figure 1c.
Figure S2. The mass spectra showing distance (reaction time)-dependence of the spontaneous oxidation of I⁻ supporting the data presented in Figure 1d.
Figure S3. Collision-induced dissociation (CID) spectra of the (a) I$_2^-$ and (b) I$_3^-$ products confirming their structures.
**Figure S4.** A typical mass spectrum showing the $\text{H}_4\text{O}_2^+$ peak, a carrier of hydroxyl radicals.
Fig. S5. A typical mass spectrum showing the oxidation products of I$^-$ of a solution of 100 μM melatonin and 100 μM NaI.